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by

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## Abstract

An external source electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer has been used to study the organometallic complexes $Ag_2(DPM)_2(BF4)_2$ (where DPM = bis-diphenylphosphino-methane), $Ag_2(DPM)_3(BF4)_2$ and $Ru(II)(bpy)_3(PF_6)_2$ (where bpy = 2,2'-bipyridyl). The high mass resolution and accurate mass assignment of parent and collisionally induced dissociation (CID) fragment ions provided structural information on these organometallic complexes. CID in the capillary/skimmer region and inside the FTICR analyzer cell were performed on these complexes and results from each type of experiment were compared. Important fragmentation pathways and reaction types, including bond cleavage, ligand loss, and ligand substitution were identified.

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## Introduction

Since the coupling of electrospray ionization (ESI) with mass spectrometry (MS) in the early 1980s by Fenn et al. (1-3), ESI/MS has become a powerful analytical tool for the analysis of a wide variety of compound types, ranging from metal ions to proteins (4-5). Intact proteins, which only a few years ago were completely inaccessible by mass spectrometry due to their high molecular weight and the requirement of a "soft" ionization method, are now routinely analyzed in the gas-phase. The multiple charging processes in the ESI source allow conventional mass spectrometers with m/z 500 to 2000 mass ranges to detect molecular masses up to 200,000 daltons (6). Because electrospray ionization occurs directly from solution at atmospheric pressure, the ions formed in the gas-phase provide information on the ions in solution (7-8). Kebarle and coworkers (4,9) have shown that ESI/MS can provide information on ion/solvent and ion/ligand interactions of alkaline earth and transition metal ions.

We have used electron impact (EI) ionization routinely to form gaseous ions from organometallic complexes in our laboratories at the University of Florida. Volatile samples are introduced into the mass spectrometer through precision leak valves and less volatile samples by heating on a solids probe (10). Since fragmentation and ligand loss are common in EI ionization, the molecular ion of interest may not be produced with this form of sample ionization (11). In addition, heating of the sample to vaporize it often leads to thermal degradation.

During the last 10-15 years, various desorption and ionization methods,

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such as field desorption (FD) (12), fast atom bombardment (FAB) (13), secondary ion (SI) (14), plasma desorption (PD) (15), electrohydrodynamic (EH) (16), laser desorption multiphoton ionization (17) and laser desorption (LD)(18) have been used to investigate larger, less volatile, organometallic complexes. These techniques have been compared by Hoffman et al. (LD versus FAB) (13a), Bjarnason et al. (LD versus EI) (18a), Bursey et al. (FAB versus FD) (13c) and Benninghoven et al. (SI versus PD) (14a). When using these ionization techniques, usually only singly charged species have been observed, even though the sample of interest can exist as a multiply charged ion in solution. These studies have shown that the ionization techniques employed produce quasimolecular ions ($[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$), can cause significant fragmentation, and produce low yields of molecular ions.

By contrast, electrospray ionization mass spectrometry (ESI/MS) produces ions directly from solution and has been shown to be an extremely soft ionization process (19). Studies by Chait et al. (7) and Kebarle et al. (4,9) have shown that ESI/MS can be used to generate intact parent ions of less volatile organometallic complexes. In addition, these studies have also shown that solution chemistry can be studied in the gas phase using ESI/MS. The mechanism of ion formation in the ESI source has been discussed by several researchers (20-22). They agree that the charging of the droplets occurs by an electrophoretic mechanism, but the mechanism of gas-phase ion production from charged droplets remains uncertain. The gas-phase ion production process was first proposed and investigated by Dole

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et al. (23). and was further investigated by Fenn et al. (24), Kebarle et al. (25a) and Guevremont et al. (25b).

Electrospray ionization sources have been successfully coupled to different types of mass spectrometers, including quadrupoles (26), magnetic sectors (27) and time of flight (28), as well as quadrupole ion traps (29) and Fourier transform ion cyclotron resonance (FTICR) spectrometers (30-31). McLafferty et al. (30a) demonstrated the utility of the high mass resolution of ESI/FTICR to resolve isotopes within charge states. ESI/FTICR can be based upon an external source design with electrospray ions formed outside the magnetic field and guided with quadrupole rods or electrostatic lenses into a trapped ion cell. An alternative approach positions the ESI source inside the high magnetic field used in the FTICR trapping and detection process. This "internal" ESI setup was first demonstrated by Laude et al. (31a). In this arrangement, ions are produced 20-25 cm from the FTICR analyzer cell, and the high magnetic field in which the ions are formed assists in focussing the ions into the cell.

In addition to high mass accuracy and ultrahigh mass resolution, the ability to perform collision-induced dissociation (CID) (32) or laser photodissociation in a FTICR mass spectrometer enhances its utility as an analytical tool. Electrospray ionization FTICR mass spectrometry further benefits from the ability to perform CID experiments in the capillary/skimmer region and/or in the FTICR analyzer cell. The potential difference between the skimmer and the capillary causes ions exiting the capillary to undergo energetic collisions with gases present in the

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capillary/skimmer region. At low values of the potential difference intact, unsolvated ions are observed. At higher values, the desolvated cations can be dissociated to give structurally informative fragment ions (33). An alternative and better approach to capillary/skimmer CID involves trapping the ions inside the FTICR analyzer cell followed by CID experiments on selectively isolated ions of interest (in-cell CID). During such in-cell CID experiments one ion is isolated by ejecting all the other ions from the FTICR analyzer/reaction cell using a series of rf pulses. The isolated ion is then excited by a single rf pulse and allowed to undergo collisions with the target gas (34). The kinetic energy gained by the ion is controlled by the duration of the rf pulse and/or its amplitude (34). The ability of the FTICR mass spectrometer to trap ions for several seconds also makes it a suitable instrument for studying ion-molecule reactions. The ion of interest can be isolated as in the CID experiment, and then a reagent gas (e.g. neutral gas of known ionization potential (IP) for charge-transfer reactions) can be introduced into the analyzer/reaction cell via a pulsed valve or precision leak valve. After a reaction delay time, the reaction products are detected.

We have been studying the reactivity of organometallic complexes in the gas phase in our laboratories at the University of Florida for the past nine years (10,35). Since EI and LD ionization were used in these investigations, the ions studied were limited to singly charged positive or negative ions. Recently, we described the use of an internal source ESI/FTICR to study organometallic complexes (31c). In the experiments reported here an external source ESI/FTICR

was used to demonstrate the applicability of this technique to study singly and doubly charged organometallic complexes. Specifically, ESI/FTICR mass spectrometry was used to study the complexes $Ru(II)(bpy)_3(PF_6)_2$ (where bpy = 2,2'-bipyridyl), $Ag_2(DPM)_2(BF_4)_2$ (where DPM = bis-diphenylphosphino-methane) and $Ag_2(DPM)_3(BF_4)_2$. Both capillary/skimmer and in-cell CID methods were used to obtain structural information for these complexes.

## Experimental

All experiments were performed using a Bruker Bio-APEX 47e mass spectrometer (36a) equipped with a 4.7 Tesla superconducting magnet, an external ion source, and a RF-shimmed Infinity analyzer cell (36b). The basic features of the external ion source FTICR mass spectrometer and the operating parameters used in these experiments have been described in detail (37). Briefly, the external ion source has two stages of differential pumping and the electrospray source has two additional stages of pumping. The electrostatic ion transfer region and the FTICR cell regions were pumped by separate 400 L/sec cryopumps and the pressure in the cell region was maintained at $4.8 \times 10^{-9}$ mbar during the electrospray operation. A 800 L/sec cryopump maintained the external ion source region pressure at $2 \times 10^{-5}$ mbar during the electrospray operation.

The ESI/FTICR system used in these experiments was equipped with an Analytica of Branford ESI source (38). This source consists of a needle operated at ground potential, a 500 um I.D. glass capillary with metalized (platinum) entrance and exit, two skimmers, three lens elements, and counter current $N_2$

drying gas. The region between the exit end of the capillary and the first skimmer was pumped by a 500 L/sec mechanical pump and the pressure in this region was maintained at 1.5 mbar. The capillary/skimmer CID experiments were performed by varying the capillary exit potential between 10 to 344 V, while holding the skimmer potential at 6 V. A second 500 L/sec mechanical pump was used to pump the region between the first skimmer and the first lens element and the pressure in this region was maintained at $4.8 \times 10^{-2}$ mbar.

All the samples studied, $(Ru(bpy)_3(PF_6)_2$, $Ag_2(DPM)_2(BF_4)_2$ and $Ag_2(DPM)_3(BF_4)_2)$, were synthesized as previously described (39-40). The samples (10 mg) were first dissolved in 0.3 mL of acetonitrile and then diluted with 0.8 mL of methanol and 0.5 mL of water. A 100 µL aliquot of this 19:31:50, acetonitrile:water:methanol solution was further diluted with 900 µL of 50:50 methanol:water before spraying. A syringe pump connected to the electrospray needle via a Teflon capillary delivered the solution with a steady flow rate of 1.2

The pulse sequence employed in this experiment has been explained in detail (37). An initial quench pulse evacuated all ions from the cell. During the ionization time ions were formed and transferred from the external source. Next, a post-ionization time allowed the ions to be thermalized. Ions were excited by the standard frequency chirp method, and 128 time-domain transients each containing 128 K data points were acquired during broad-band detection (100 - 2000 amu). For CID experiments, following the post-ionization delay, the ion of interest was isolated using a series of ion ejection sweeps. Collision-induced

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dissociation was carried out on the isolated ion by employing an excitation pulse of a fixed amplitude (36 $V_{p-p}$), but variable duration, at the cyclotron frequency of the ion. The isolated excited ion was then allowed to collide with the collision gas for 500 ms. Air (collision gas) was introduced into the vacuum chamber to a pressure of 5 x $10^{-7}$ mbar above the background pressure.

## Results

To obtain structural information on the three complexes ($Ag_2(DPM)_2(BF_4)_2$, $Ag_2(DPM)_3(BF_4)_2$ and $Ru(bpy)_3(PF_6)_2$) being studied, a series of experiments was performed using CID in the region between the capillary exit and the first skimmer. Tables 1, 2 and 3 give the CID results for ions formed from $Ag_2(DPM)_2(BF_4)_2$, $Ag_2(DPM)_3(BF_4)_2$ and $Ru(bpy)_3(PF_6)_2$, respectively. Figures 1, 2 and 3 show the ESI/FTICR mass spectra of these complexes for two of the capillary/skimmer CID energies. Mass spectra 1a, 2a and 3a were obtained with a CID energy of 29 V (skimmer at 6 V and capillary at 35 V) and 1b, 2b and 3b were obtained with a CID energy of 244 V (skimmer at 6 V and capillary at 250 V). Silver and ruthenium have more than one isotope, with the most abundant isotopes of mass 107 and 102 Da, respectively. For the purpose of clarity, $^{107}Ag$ and $^{102}Ru$ will be used when referring to the masses of various organometallic complexes. To confirm the structural information obtained using the capillary/skimmer CID, a series of in-cell CID experiments was performed on isolated ions. Table 4 gives the in-cell CID results for $[Ag_2(DPM)_2CH_3COO]^+$ and $[Ag_2(DPM)_2]^{2+}$; the results for $[Ru(bpy)_3]^{2+}$ are presented in Table 5.

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## Discussion

### a) Capillary/skimmer CID

Although capillary/skimmer CID is a convenient method to obtain structural information of organometallic complexes, when using this technique it is not possible to determine unambiguously the fragments arising from a specific ion. In addition, ions entering the capillary/skimmer region have a much broader kinetic energy distribution than ions entering the FTICR analyzer cell, and thus bond energy estimations cannot be obtained from CID experiments. As shown in Table 1 and Figure 1a, at a lower capillary/skimmer potential (29 V), collisional activation is low and peaks (decreasing intensity) due to $[Ag_2(DPM)_2CH_3COO]^+$ (m/z 1041), $[Ag_2(DPM)_2]^{2+}$ (m/z 491), $[Ag_2(DPM)_2(BF_4)]^+$ (m/z 1069) and $[Ag_2(DPM)_2Cl]^+$ (m/z 1017) were observed when $[Ag_2(DPM)_2(BF_4)_2$ was electrosprayed (where DPM = $(C_6H_5)_2P\text{-}CH_2\text{-}P(C_6H_5)_2$). The doubly charged ions were easily identified, since peaks occurred with half-mass separation at the expected mass/charge (m/z) range and with the expected isotopic abundances. The singly charged ions, $[Ag_2(DPM)_2CH_3COO]^+$ (m/z 1041), $[Ag_2(DPM)_2(BF_4)]^+$ (m/z 1069), and $[Ag_2(DPM)_2Cl]^+$ were presumably formed by anion ($CH_3COO^-$, $BF_4^-$ and $Cl^-$) addition to the silver complex in solution. The acetate and chloride anions are present as impurities in the solution.

At 74 V of activation, the mass spectrum showed a peak due to a mixture of $[Ag_2(DPM)_2]^{2+}$ and $[Ag(DPM)]^+$ both at m/z 491. The identity of this mixture can be verified (*vide infra*) from the shifting of the relative intensities of the

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isotope peaks from (26.9:49.9:23.2) expected for an ion containing two silver atoms to one more closely approaching that (51.8:48.2) expected for an ion containing only one silver atom. In addition, peaks due to $[Ag_2(DPM)_2]^+$ (m/z 982) and $[Ag_2(DPM)_2Cl]^+$ (m/z 1017) were also observed. As shown in Table 1, at an activation energy of 119 V all doubly charged ions dissociated to give structurally informative fragment ions, and $[Ag_2(DPM)_2]^+$ (m/z 982) was observed as the most intense peak in the spectrum. In addition, ions such as $[Ag(DPM)]^+$ (m/z 491), $[Ag(DPM)_2]^+$ (m/z 875), and $[Ag(DPM)_2Cl]^+$ (m/z 910), each containing one silver atom, were also observed in the spectrum. At an activation energy of 154 V a peak due to loss of a DPM ligand from $[Ag_2(DPM)_2CH_3COO]^+$ (m/z 1041) was observed as the most intense peak in the spectrum and DPM dissociated to produce $[DPM\text{-}P(C_6H_5)_2]^+$ at m/z 199. As shown in Figure 1b, increasing the activation energy to 244 V produced $[Ag(DPM)]^+$ (m/z 491) as the intense peak, and DPM further dissociated to give structurally informative peaks such as $[(DPM)\text{-}CH_2P(C_6H_5)_2]^+$ (m/z 185) and $[(DPM)\text{-}P(C_6H_5)_3H]^+$ (m/z 121). At the highest activation energy used, 344 V, fragments due to dissociation of DPM appeared as most intense peaks.

The capillary/skimmer CID of $Ag_2(DPM)_3(BF_4)_2$ parallels that of the $Ag_2(DPM)_2(BF_4)_2$. The observed dissociation pathways for this ion are listed in Table 2. At 29 V of activation, the CID processes are negligible, and $[Ag_2(DPM)_3]^{2+}$ (m/z 683) was observed as the most intense peak (Figure 2a). Other ions observed included $[Ag_2(DPM)_2CH_3COO]^+$ (m/z 1041), $[Ag_2(DPM)_3Cl]^+$

(m/z 1401), $[Ag_2(DPM)_3BF_4]^+$ (m/z 1453), $[Ag_2(DPM)_3CH_3COO]^+$ (m/z 1425), $[Ag_2(DPM)_2BF_4]^+$ (m/z 1069) and $[Ag(DPM)_2]^+$ (m/z 875) (due to anion adduction and/or some fragmentation). Increasing the capillary potential to 80 V promoted dissociation to form $[Ag_2(DPM)]^{2+}/[Ag(DPM)]^+$ at m/z 491. In addition, all $[Ag_2(DPM)_3X]^+$ (where X= Cl⁻, $BF_4^-$ and $CH_3COO^-$) ions dissociated to produce $[Ag_2(DPM)_2X]^+$ ions. As observed for $Ag_2(DPM)_2(BF_4)_2$ at 119 V, all doubly charged ions dissociated and ions containing a single silver atom were observed in the spectrum. At an activation energy of 154 V, DPM dissociated to give $[(DPM)-P(C_6H_5)_2]^+$ (m/z 199), and ions due to loss of a DPM ligand from $[Ag_2(DPM)_2X]^+$ were observed in the spectrum ($[Ag_2(DPM)CH_3COO]^+$ (m/z 657) and $[Ag_2(DPM)Cl]^+$ (m/z 633)). As shown in Figure 2b, at activation energies higher than 154 V, DPM further dissociated to give structurally informative ions such as $[(DPM)-P(C_6H_5)_3H]^+$ (m/z 121), $[(DPM)-P(C_6H_5)_2]^+$ (m/z 199) and $[(DPM)-CH_2P(C_6H_5)_2]^+$ (m/z 185).

Presence of ions containing a single silver atom and the absence of $Ag_2^+$ in the spectrum suggest that there are no bonds between the silver atoms in $Ag_2(DPM)_2(BF_4)_2$ and $Ag_2(DPM)_3(BF_4)_2$. This conclusion is reinforced by X-ray crystallographic studies (40b) which give 3.105 Å as the Ag--Ag distance in $Ag_2(DPM)_3(BF_4)_2$. Previous work on complexes containing two silver atoms has been inconclusive regarding the existence of metal-metal bonds. Busch et al. (41) examined the silver salts of acetic acid, propionic acid and benzoic acid using SI and EI ionization. In that study ions such as $Ag_2X^+$ (where X is H, O, OH, $CH_3$, $CH_3COO$, and $CH_3COOCH_2$) were formed and analyzed by tandem mass

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spectrometry. All of the $Ag_2X^+$ ions except $Ag_2H^+$ and $Ag_2OH^+$ dissociated to give $Ag_2^+$. This observation led the authors to conclude that, with the exception of $Ag_2H^+$ and $Ag_2OH^+$, all of the $Ag_2X^+$ contained metal-metal bonds. These experimental findings were not supported theoretically by Dekock et al. (42), who used Hartree-Fock calculations to study $Ag_2H^+$ and $Ag_2CH_3^+$. They predicted that both of these ions contain metal-metal bonds. However, a study of $Ag_2H^+$ by Gaspar et. al (43) used a simple molecular pseudopotential method and concluded that this ion does not contain any metal-metal bonds.

Capillary/skimmer CID results for $Ru(bpy)_3(PF_6)_2$ are summarized in Table 3 (where bpy = $(NH_4C_5)-(C_5H_4N)$). As shown in Figure 3a, at an activation energy of 29 V $[Ru(bpy)_3]^{2+}$, m/z 285, was the most intense peak in the mass spectrum. In addition, peaks due to $[Ru(bpy)_3PF_6]^+$ (m/z 715), $[Ru(bpy)_3(PF_6)_2Na]^+$ (m/z 883) and $[Ru(bpy)_3CH_3COO]^+$ (m/z 629) were also observed. Increasing the capillary potential to 80 V produced $[Ru(bpy)_2]^{2+}$ (m/z 207) and $[Ru(bpy)_2CH_3COO]^+$ (m/z 473), corresponding to the loss of one bipyridyl ligand from $[Ru(bpy)_3]^{2+}$ (m/z 285) and $[Ru(bpy)_3CH_3COO]^+$ (m/z 629), respectively. At an activation energy of 119 V dissociation of $PF_6^-$ ($PF_6^-$ ---> $PF_5$ + $F^-$) is evident from the presence of $[Ru(bpy)_2F]^+$ at m/z 433. At higher activation energies decaying intensity for $[Ru(bpy)_2]^{2+}$ (m/z 207) and increasing intensity for $[Ru(bpy)_2F]^+$ (m/z 433) indicate that $[Ru(bpy)_2F]^+$ is forming from $[Ru(bpy)_2]^{2+}$. Structurally informative peaks corresponding to $[(bpy)+H]^+$ (m/z 157), $[Ru(bpy)]^+$ (m/z 258) and $[Ru(bpy)_3]^+$ (m/z 570) were also observed in the mass spectrum. At an activation energy of 154 V

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[Ru(bpy)$_3$(PF$_6$)$_2$Na]$^+$ disappears, and new peaks due to [Ru(bpy)$_2$C$_5$H$_4$N]$^+$ (m/z 492) and [Ru(bpy)$_2$]$^+$ (m/z 414) appear in the spectrum. As shown in Figure 3b, at 244 V of activation the fluoride ion is apparently retained when the loss of bipyridyl ligand occurs from [Ru(bpy)$_2$F]$^+$ to form [Ru(bpy)F]$^+$ at m/z 277. In addition, a peak corresponding to [Ru(bpy)C$_5$H$_4$N]$^+$ at m/z 336 was observed in the spectrum. Detection of ions containing the pyridyl group (C$_5$H$_4$N), in fragments such as [Ru(bpy)$_2$C$_5$H$_4$N]$^+$ (m/z 492), [Ru(bpy)C$_5$H$_4$N]$^+$ (m/z 336) and [RuC$_5$H$_4$N]$^+$ (m/z 180) suggests that C-C bond cleavage is occurring in the bipyridyl ligand.

As to the formation of [(bpy)+H]$^+$, we speculate that [(bpy)+H]$^+$ is formed from the gas phase reaction of [Ru(bpy)$_2$]$^{2+}$ with background water ([Ru(bpy)$_2$]$^{2+}$(m/z 207) + H$_2$O ---> [Ru(bpy)]$^+$ (m/z 258) + [(bpy)+H]$^+$ (n./.. 157) + OH$^-$). The formation of [(bpy)+H]$^+$ from Fe(bpy)$_3$(SO$_4$) and Ni(bpy)$_3$(SO$_4$) has been studied in detail by Turecek et al. (44), using an electrospray ionization double-focusing mass spectrometer. Their results led to the conclusion that [(bpy)+H]$^+$ is due to solution chemistry and not due to reaction of the complex ions in the gas phase. The study by Turecek et al. (44) contrasts with the CID study of Chait et al. (7b) and our ESI/FTICR study on Ru(bpy)$_3$(PF$_6$)$_2$. Our speculation that [(bpy)+H]$^+$ is forming from the reaction of [Ru(bpy)$_2$]$^{2+}$ with background water is further confirmed using the in-cell CID method, which will be discussed in the next section.

In a study by Freas et al.(45) FAB was used to obtain structural information on [Ru(bpy)$_2$(typ)](PF$_6$)$_2$ and [Ru(bpy)$_2$(bdmt)](PF$_6$)$_2$ (where typ = 2,2':6,2"-

terpyridine and bdmt = 3,3':5,3"-bis(bimethylene)-2,2':6,2"-terpyridine). In that study the highest mass ions observed included $[Ru(bpy)_2(bdmt)PF_6]^+$ (m/z 844), and $[Ru(bpy)_2(tpy)PF_6]^+$ (m/z 792), corresponding to the loss of a $PF_6^-$ counterion. In addition, peaks corresponding to the doubly charged ions $[Ru(bpy)_2(bdmt)]^{2+}$ and $[Ru(bpy)_2(tpy)]^{2+}$ were observed. The fragmentation pathway suggested for the formation of $[Ru(bpy)(bdmt)F]^+$, $[Ru(bpy)(tpy)F]^+$ and $[Ru(bdmt)F]^+$ resembles that of the $[Ru(bpy)_2F]^+$ and $[Ru(bpy)F]^+$ observed in our ESI/FTICR study. The absence of $[Ru(bpy)_2(bdmt)F]^+$ led Freas et al. to conclude that the fluoride ion is an inner-sphere ligand, and that fluoride-containing ions arise from the gas-phase dissociation of $PF_6^-$ in the FAB source. These observations by Freas et al. corroborate the results obtained using ESI/FTICR ($[Ru(bpy)_3F]^+$ and $[Ru(phen)_3F]^+$ were not observed) on $[Ru(bpy)_3](PF_6)_2$ and $[Ru(phen)_3](PF_6)_2$ (46) (where phen = 1,10-phenanthroline).

**b) In-Cell CID**

Although numerous speculations can be made from capillary/skimmer CID data, the results are often not conclusive, because the identity of parent ions undergoing dissociation is not known. Thus, a particular fragment might arise from two or more parents, or from a different parent than appears most likely. In an attempt to obtain more detailed structural information from unambiguous fragmentation pathways, in-cell CID experiments were carried out on $[Ag_2(DPM)_2CH_3COO]^+$, $[Ag_2(DPM)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$. Since the ion of interest is isolated in the FTICR analyzer cell prior to CID, this technique is more reliable

for deducing structural information. Using this method allows several questions to be addressed. (1) Is the $[Ag_2(DPM)_x+59]^+$ (where X = 1, 2, and 3) due to the addition of $CH_3COO^-$ or to solvation with $CH_3CN$ and $H_2O$ ? (2) Do $[Ag_2(DPM)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ undergo reduction to form $[Ag_2(DPM)_2]^+$ and $[Ru(bpy)_3]^+$, respectively ? (3) Is $[Ru(bpy)_xF]^+$ produced from the dissociation of $PF_6^-$ or by some other mechanism? (4) Is $[(bpy+H]^+$ due to CID of $[Ru(bpy)_3]^+$ in the gas phase or from some other solution chemistry?

As shown in Table 4, results from in-cell CID of $[Ag_2(DPM)_2+59]^+$ (m/z 1041) suggest that mass 59 arises from $CH_3COO^-$ and not from solvation with $CH_3CN$ and $H_2O$. If mass 59 were due to $CH_3CN$ and $H_2O$, CID of m/z 1041 would have produced fragment ions at m/z 1000 and/or 1023. Increasing the CID pulse width from 0.3 to 1 μs produced $[Ag_2(DPM)_2]^+$ as a quite intense peak. Further increase in the CID energy produced a peak due to $[Ag_2(DPM)+59]^+$ and peaks corresponding to addition of $CH_3CN$ and/or $H_2O$ were absent from the spectrum.

Results from the in-cell CID of $[Ag_2(DPM)_2]^{2+}$ (m/z 491) are also shown in Table 4. When the CID pulse width was 0.3 μs, the parent was still observed as the most intense peak. Increasing the CID pulse width from 0.3 to 1 μs produced a mixture of $[Ag_2(DPM)_2]^{2+}/[Ag(DPM)]^+$ at m/z 491 and fragments due to dissociation of DPM ($[(DPM)-P(C_6H_5)_3H]^+$ (m/z 121) and $[(DPM)-P(C_6H_5)_2]^+$) (m/z 199) were observed in the spectrum. When the CID pulse width was increased to 10 μs, $[Ag(DPM)]^+$ (m/z 491) was observed as the most intense peak. Results from these CID experiments indicate tha

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t no reduction reaction is occurring. If reduction had occurred, a peak due to $[Ag_2(DPM)_2]^+$ (m/z 982) should have been observed in the results.

The high mass resolution capabilities of FTICR have long been identified as one of the analytical advantages of the technique in comparison with other mass spectrometers. In 1983, Wanczek et al. (47) used a 4.7 Tesla magnet and a background pressure of $8 \times 10^{-11}$ mbar to achieve a resolution in excess of $10^8$ for water. Recently, McLafferty et al. (48) and Smith et. al (49) have shown that ultrahigh resolution can be achieved with ESI/FTICR. The advantage of using a high mass resolution instrument for CID experiments is shown from the results on $[Ag_2(DPM)_2]^{2+}$ (m/z 491). Since $[Ag_2(DPM)_2]^{2+}$ and $[Ag(DPM)]^+$ both occur at a nominal m/z of 491, it would be a difficult task to differentiate between $[Ag_2(DPM)_2]^{2+}$ and $[Ag(DPM)]^+$ without a routine resolution of 0.5 amu. Figure 4 gives further indications of the importance of the high mass resolution in the analysis of organometallic complexes. Figure 4a illustrates the results obtained with a minimum energy deposition (CID pulse width = 0.3 µs) into the parent ion $([Ag_2(DPM)_2]^{2+})$. At this CID energy peaks at m/z 491, 492 and 493 are due to $[^{107}Ag^{107}Ag(DPM)_2]^{2+}$, $[^{107}Ag^{109}Ag(DPM)_2]^{2+}$ and $[^{109}Ag^{109}Ag(DPM)_2]^{2+}$, respectively. Peaks occurring at m/z 491.5, 492.5 and 493.5 are due to the presence of carbon-13 isotopes. Increasing the CID pulse width from 0.3 to 10 µs deposits more energy into the parent ion and produces more fragmentation. Figure 4e illustrates the results obtained with a CID pulse width of 10 µs; at this CID energy fragment ions due to $[^{107}Ag(DPM)]^+$ and $[^{109}Ag(DPM)]^+$ were observed

at m/z 491 and 493, respectively.

Results from in-cell CID of $[Ru(bpy)_3]^{2+}$ (m/z 285) are given in Table 5. Increasing the CID pulse width from 0.3 to 7 $\mu s$ produced $[Ru(bpy)_2]^{2+}$ (m/z 207) as the major fragment ion. Further increase of the CID pulse width from 7 $\mu s$ to 10 $\mu s$ produced fragment ions due to $[Ru(bpy)_2]^{2+}$ (m/z 207), $[Ru(bpy)]^+$ (m/z 258) and $[(bpy)+H]^+$ (m/z 157). When more energy was imparted to the $[Ru(bpy)_3]^{2+}$ ion (pulse width of 15 $\mu s$), all the doubly charged ions dissociated to give $[Ru(bpy)]^+$ and $[(bpy)+H]^+$.

As described by Freas et al. (45), the loss of a bipyridyl ligand from $[Ru(bpy)_3]^{2+}$ opens one or two coordination sites in the hexacoordinated Ru(II) complex and the availability of $F^-$ produced from the dissociation of $PF_6^-$ then leads to the formation of $[Ru(bpy)_2F]^+$ (m/z 433). The question arises as to the mechanism of formation of $[Ru(bpy)F]^+$ (m/z 277). One possibility is the simple loss of a bipyridyl ligand from $[Ru(bpy)_2F]^+$. Another possibility is formation of $[Ru(bpy)]^{2+}$ followed by complexation with $F^-$ to form $[Ru(bpy)F]^+$. However, the latter pathway can be ruled out, because $[Ru(bpy)]^{2+}$ was not present in the capillary/skimmer CID experiments. In addition, the results presented here indicate that there is no reduction occurring in these reactions. This observation supports the results obtained by Chait et al. (7b) and Cook et al. (16) for $[Ru(bpy)_3]Cl_2$. However, ligand exchange reactions between the $[Ru(bpy)_3]^{2+}$ and $Cl^-$ or solvent, as reported in detail above, were not observed in the earlier studies.

In-cell CID of $[Ru(bpy)_3]^{2+}$ produces $[(bpy)+H]^+$ as one of the fragment ions.

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Since all other ions were ejected from the analyzer cell, $[(bpy)+H]^+$ must be formed by the reaction of $[Ru(bpy)_2]^{2+}$ with background water or water present in the collision gas. If $[(bpy)+H]^+$ were preformed in the solution as Turecek et al. (44) observed in their study, at lower capillary/skimmer CID energies, a peak due to $[(bpy)+H]^+$ should have been observed along with $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3PF_6]^+$. Thus, the in-cell CID of $[Ru(bpy)_3]^{2+}$ suggests that the formation of $[(bpy)+H]^+$ is due to ion/molecule reaction of the $[Ru(bpy)_2]^{2+}$ in the gas phase. As shown in Table 5, the formation of $[Ru(bpy)]^+$ (m/z 258) and $[(bpy)+H]^+$ (m/z 157) and the disappearance of $[Ru(bpy)_2]^{2+}$ (m/z 207) with a CID pulse width of 10 μs suggests that the precursor for $[(bpy)+H]^+$ is $[Ru(bpy)_2]^{2+}$.

## Conclusions

The highest mass ion observed for $Ag_2(DPM)_3(BF_4)_2$ and $Ag_2(DPM)_2(BF_4)_2$ corresponded to $[Ag_2(DPM)_nBF_4]^+$ (where n is 2 and 3). Abundant doubly charged ions ($[Ag_2(DPM)_3]^{2+}$ and $[Ag_2(DPM)_2]^{2+}$) were observed at lower activation energies. Dissociation pathways were charge independent, and predominant fragment ions were due to losses of DPM ligands. At higher activation energies products due to dissociation of DPM ligand were observed in the spectra. In-cell CID experiments on $[Ag_2(DPM)_2]^{2+}$ demonstrated the advantage of using a high mass resolution mass spectrometer to study organometallic complexes.

The highest mass ion observed for $Ru(bpy)_3(PF_6)_2$ corresponded to $[Ru(bpy)_3PF_6]^+$ (m/z 715). Abundant $[Ru(bpy)_3]^{2+}$ was observed at 29 and 74 V of capillary/skimmer activation. The predominant fragment ions in the

capillary/skimmer CID spectra are due to losses of intact bipyridyl ligands and $PF_5$. Higher activation energies produced fragments due to C-C bond cleavage from the bipyridyl ligand.

The results of this study suggest that ESI/FTICR can be an important tool in the study of organometallic complexes. In addition, capillary/skimmer and in-cell CID methods are useful for the determination of the fragmentation pathways of organometallic complexes.

## Acknowledgements

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Table 1. Capillary/Skimmer CID results for $Ag_2(DPM)_2(BF_4)_2$

| Ions Detected (m/z) | Capillary/skimmer CID energy (v) | | | | | |
|---|---|---|---|---|---|---|
| | 29 | 74 | 119 | 154 | 244 | 344 |
| $[Ag_2(DPM)_2]^{2+}$ (491) | 13[a] | | | | | |
| $[Ag_2(DPM)_2BF_4]^+$ (1069) | 30 | 3 | 6 | 1 | | |
| $[Ag_2(DPM)_2CH_3COO]^+$ (1041) | 100 | 100 | 58 | 1 | 1 | 7 |
| $[Ag_2(DPM)_2Cl]^+$ (1017) | | 2 | 2 | | | |
| $[Ag_2(DPM)_2]^+$ (982) | | 13 | 100 | 26 | 2 | 18 |
| $[Ag(DPM)_2Cl]^+$ (910) | | | 1 | | | |
| $[Ag(DPM)_2]^+$ (875) | | 7 | 7 | 1 | | |
| $[Ag_2(DPM)C_6H_5]^+$ (675) | | | | | 5 | 7 |
| $[Ag_2(DPM)CH_3COO]^+$ (657) | | | 59 | 100 | 8 | 11 |
| $[Ag_2(DPM)Cl]^+$ (633) | | | | 1 | | |
| $[Ag_2(DPM)]^+$ (598) | | | | | 2 | |
| $[Ag_2(DPM)_2]^{2+}/[Ag(DPM)]^+$ (491) | | 31 | | | | |
| $[Ag(DPM)]^+$ (491) | | | 24 | 9 | 100 | 63 |
| $[(DPM)-P(C_6H_5)_2]^+$ (199) | | | | 2 | 25 | 65 |
| $[(DPM)-CH_2P(C_6H_5)_2]^+$ (185) | | | | | | 82 |
| $[(DPM)-P(C_6H_5)_3H]^+$ (121) | | | | | 12 | 100 |

a = Relative abundance

Table 2. Capillary/Skimmer CID results for $Ag_2(DPM)_3(BF_4)_2$

| Ions Detected (m/z) | Capillary/skimmer CID energy (v) | | | | | |
|---|---|---|---|---|---|---|
| | 29 | 74 | 119 | 154 | 244 | 344 |
| $[Ag_2(DPM)_3]^{2+}$ (683) | 100[a] | 19 | | | | |
| $[Ag_2(DPM)_3BF_4]^+$ (1453) | 6 | 2 | | | | |
| $[Ag_2(DPM)_3CH_3COO]^+$ (1425) | 5 | 3 | | | | |
| $[Ag_2(DPM)_3Cl]^+$ (1401) | 6 | 5 | | | | |
| $[Ag_2(DPM)_2BF_4]^+$ (1069) | 3 | 11 | 13 | 11 | | |
| $[Ag_2(DPM)_2CH_3COO]^+$ (1041) | 13 | 27 | 18 | 8 | 2 | 5 |
| $[Ag_2(DPM)_2Cl]^+$ (1017) | | 7 | 12 | 12 | | |
| $[Ag_2(DPM)_2]^+$ (982) | | | 8 | 17 | 12 | 10 |
| $[Ag(DPM)_2]^+$ (875) | 2 | 58 | 37 | 13 | 7 | 23 |
| $[Ag_2(DPM)C_6H_5]^+$ (675) | | | | | 19 | |
| $[Ag_2(DPM)CH_3COO]^+$ (657) | | | 5 | 23 | 27 | 7 |
| $[Ag_2(DPM)Cl]^+$ (633) | | | | 2 | 25 | |
| $[Ag(DPM)]^+$ (491) | | | 100 | 100 | 100 | 100 |
| $[Ag_2(DPM)_2]^{2+}/[Ag(DPM)]^+$ (491) | | 100 | | | | |
| $[(DPM)-P(C_6H_5)_2]^+$ (199) | | | | 7 | 15 | 95 |
| $[(DPM)-CH_2P(C_6H_5)_2]^+$ (185) | | | | | | 33 |
| $[(DPM)-P(C_6H_5)_3]^+$ (121) | | | | | 10 | 70 |

a = Relative abundance

Table 3. Capillary/Skimmer CID results for Ru(bpy)$_3$(PF$_6$)$_2$

| Ions Detected (m/z) | Capillary/skimmer CID energy (v) | | | | | |
|---|---|---|---|---|---|---|
| | 29 | 74 | 119 | 154 | 244 | 344 |
| [Ru(bpy)$_3$]$^{2+}$ (285) | 100[a] | 100 | 24 | 9 | | |
| [Ru(bpy)$_2$]$^{2+}$ (207) | | 2 | 67 | 8 | | |
| [Ru(bpy)$_3$(PF$_6$)$_2$Na]$^+$ (883) | 5 | 5 | 3 | | | |
| [Ru(bpy)$_3$PF$_6$]$^+$ (715) | 75 | 63 | 100 | 100 | 100 | 83 |
| [Ru(bpy)$_3$CH$_3$COO]$^+$ (629) | 3 | 3 | | | | |
| [Ru(bpy)$_3$]$^+$ (570) | | | 7 | 27 | 38 | 57 |
| [Ru(bpy)$_2$C$_5$H$_4$N]$^+$ (492) | | | | 9 | 15 | 22 |
| [Ru(bpy)$_2$CH$_3$COO]$^+$ (473) | | 3 | 3 | 4 | 4 | 3 |
| [Ru(bpy)$_2$F]$^+$ (433) | | | 23 | 97 | 74 | 100 |
| [Ru(bpy)$_2$]$^+$ (414) | | | | 26 | 82 | 54 |
| [Ru(bpy)C$_5$H$_4$N]$^+$ (336) | | | | | 45 | 19 |
| [Ru(bpy)F]$^+$ (277) | | | | | 28 | 7 |
| [Ru(bpy)]$^+$ (258) | | | 9 | 5 | 12 | 11 |
| [RuC$_5$H$_4$N]$^+$ (180) | | | | | | 17 |
| [(bpy)+H]$^+$ (157) | | | 22 | 16 | | |

a = Relative abundance

Table 4. In-cell CID of $[Ag_2(DPM)_2CH_3COO]^+$ and $[Ag_2(DPM)_2]^{2+}$

| Precursor ion | CID pulse width($\mu s$) | Ions Detected (Decreasing Intensity) | (m/z) |
|---|---|---|---|
| $[Ag_2(DPM)_2CH_3COO]^+$ | 0.3 | $[Ag_2(DPM)_2CH_3COO]^+$ | 1041 |
| | 1 | $[Ag_2(DPM)_2]^+$ | 982 |
| | | $[Ag_2(DPM)_2CH_3COO]^+$ | 1041 |
| | | $[Ag_2(DPM)C_6H_5]^+$ | 675 |
| | | $[Ag_2(DPM)CH_3COO]^+$ | 657 |
| | 2 | $[Ag_2(DPM)C_6H_5]^+$ | 675 |
| | | $[Ag_2(DPM)_2]^+$ | 982 |
| | | $[Ag(DPM)]^+$ | 491 |
| | | $[Ag_2(DPM)CH_3COO]^+$ | 657 |
| | | $[Ag_2(DPM)_2CH_3COO]^+$ | 1041 |
| | | $[(DPM-P(C_6H_5)_3H]^+$ | 121 |
| | 5 | $[Ag(DPM)]^+$ | 491 |
| | | $[Ag_2(DPM)C_6H_5]^+$ | 675 |
| | | $[Ag_2(DPM)_2]^+$ | 982 |
| | | $[(DPM-P(C_6H_5)_3H]^+$ | 121 |
| | | $[Ag_2(DPM)CH_3COO]^+$ | 657 |
| | 10 | $[(DPM-P(C_6H_5)_3H]^+$ | 121 |
| | | $[Ag(DPM)]^+$ | 491 |
| $[Ag_2(DPM)_2]^{2+}$ | 0.3 | $[Ag_2(DPM)_2]^{2+}$ | 491 |
| | 1 | $[Ag_2(DPM)_2]^{2+}/[Ag(DPM)]^+$ | 491 |
| | | $[(DPM)-P(C_6H_5)_2]^+$ | 199 |
| | | $[(DPM)-P(C_6H_5)_3H]^+$ | 121 |
| | | $[DPM]^+$ | 384 |
| | 2 | $[Ag_2(DPM)_2]^{2+}/[Ag(DPM)]^+$ | 491 |
| | | $[(DPM)-P(C_6H_5)_2]^+$ | 199 |
| | | $[(DPM)-P(C_6H_5)_3H]^+$ | 121 |
| | | $[DPM]^+$ | 384 |
| | 5 | $[Ag_2(DPM)_2]^{2+}/[Ag(DPM)]^+$ | 491 |
| | | $[(DPM)-P(C_6H_5)_2]^+$ | 199 |
| | | $[(DPM)-P(C_6H_5)_3H]^+$ | 121 |
| | | $[DPM]^+$ | 384 |
| | 10 | $[Ag(DPM)]^+$ | 491 |
| | | $[(DPM)-P(C_6H_5)_2]^+$ | 199 |
| | | $[(DPM)-P(C_6H_5)_3H]^+$ | 121 |
| | | $[DPM]^+$ | 384 |

**Table 5.** In-cell CID of $[Ru(bpy)_3]^{2+}$

| Precursor ion | CID pulse width($\mu$s) | Ions Detected (Decreasing intensity) | (m/z) |
|---|---|---|---|
| $[Ru(bpy)_3]^{2+}$ | 0.3 | $[Ru(bpy)_3]^{2+}$ | 285 |
| | 3 | $[Ru(bpy)_3]^{2+}$ | 285 |
| | 7 | $[Ru(bpy)_3]^{2+}$ | 285 |
| | | $[Ru(bpy)_2]^{2+}$ | 207 |
| | 10 | $[Ru(bpy)_3]^{2+}$ | 285 |
| | | $[Ru(bpy)_2]^{2+}$ | 207 |
| | | $[(bpy)+H]^+$ | 157 |
| | | $[Ru(bpy)]^+$ | 258 |
| | 12 | $[(bpy)+H]^+$ | 157 |
| | | $[Ru(bpy)_2]^{2+}$ | 207 |
| | | $[Ru(bpy)_3]^{2+}$ | 285 |
| | | $[Ru(bpy)]^+$ | 258 |
| | 15 | $[(bpy)+H]^+$ | 157 |
| | | $[RuC_{10}H_8]^+$ | 230 |
| | | $[Ru(bpy)]^+$ | 258 |
| | | $[RuC_{10}H_8N]^+$ | 244 |

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## Figure Captions:

Figure 1. Electrospray ionization mass spectra of $[Ag_2(DPM)_2](BF_4)_2$ obtained with capillary/skimmer CID energy of (a) 29 V and (b) 244 V.

Figure 2. Electrospray ionization mass spectra of $[Ag_2(DPM)_3](BF_4)_2$ obtained with capillary/skimmer CID energy of (a) 29 V and (b) 244 V.

Figure 3. Electrospray ionization mass spectra of $[Ru(bpy)_3](PF_6)_2$ obtained with capillary/skimmer CID energy of (a) 29 V and (b) 244 V.

Figure 4. Mass spectra from in-cell CID of $[Ag_2(DPM)_2]^{2+}$. CID pulse width was (amplitude was 36 $V_{p-p}$): (a) 0.3 µs; (b) 1 µs; (c) 2 µs; (d) 5 µs; and (e) 10 µs.